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## ESTABLISHING THE NATURE OF KINETIC EFFECTS OF THE HIGH-TEMPERATURE OXIDATION (COMBUSTION) PROCESS OF SOME LIQUID ORGANIC MATTERS BY ACOUSTIC RADIATION

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In this article, the results of the study on the physicochemical characteristics of some liquid organic matters on the kinetics of their high-temperature oxidation (combustion) were presented for the first time. These results were obtained by the method of acoustic emission spectrum from heat source. The research results of the amplitude-time characteristics (until cessation of combustion completely) and the frequency response functions (in a given frequency range) of oxidation (combustion) process of liquid organic matters showed that there are following unambiguous dependences: 1) the dependences of the number of the amplitude maximum of the frequency and time spectrum in a given frequency range, as well as of the fractal dimension of the received acoustic signal on the number of carbon atoms in the carbon frame of organic matters and their molar mass; and 2) the dependences of the time of beginning of the combustion (ignition) of primary cloud of organic matters vapors and the final combustion time of the primary cloud of organic matters vapors on the number of carbon atoms in the carbon frame of the organic matters and their partial vapor pressures. The practical aspect of using the results obtained is dictated by the need to develop standard samples of amplitude-time and amplitude-frequency characteristics, depending on the physicochemical and combustible properties of the organic matters. This is necessary for the data bank of the acoustic emission monitoring system to establish a fire hazardous state and make anti-crisis decisions at critical infrastructure facilities.

**Keywords:** high-temperature oxidation, combustion, acoustic emission analysis, physicochemical characteristics, frequency response functions; reliability, spectrogram, acoustic emission monitoring.

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### Introduction

At present, the method of acoustic emission (AE) has reached a fairly high level of development in the diagnosis of the strength solids and the dynamics of processes in liquid mediums. Therefore, the AE method in its polyfunctionality fully corresponds to the research of the homogeneous kinetics and heterogeneous chemical reactions and technological processes in liquid media [1,2]. Thus, the AE method fully corresponds in its multifunctionality to the tool for studying the kinetics of homogeneous and

heterogeneous chemical reactions, technological processes in liquid media. That method allows researching the following: chemical processes at the micro- and macromolecular level [3,4]; crystallization kinetic and electro-crystallization processes, dissolution, and melting of crystals of metals, inorganic and organic compounds in solvents of various nature [5,6]. The results of previous researches open up wide opportunities for improving methods for controlling physicochemical processes in liquid medium, non-destructive testing methods of materials and products

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*Establishing the nature of kinetic effects of the high-temperature oxidation (combustion) process of some liquid organic matters by acoustic radiation*

of production for various purposes, of the emergence dynamics of specific and environmentally hazardous physical and chemical processes in functioning industries [7–10].

Meanwhile, in the scientific and technical literature there are still no works on the research of the high-temperature oxidation (combustion) kinetics of liquid organic matters (OM), which were carried out using the AE method.

The processes of high-temperature oxidation of liquid combustible materials are accompanied by an outbreak of primary OM vapors and the destruction of their initial molecular crystal structure. This leads to the occurrence of critical internal stresses thermal volumetric physical and chemical effects, and phase transitions.

Therefore, the tools for researching the kinetics of the combustion reactions of OM should fix a set of characteristics describing the individual features of the process high-temperature staged oxidation. These tools are necessary to replenish the data bank of the monitoring system critical infrastructure objects with a massive stay of people and combustible materials of nature various physical and chemical [11–13].

Earlier, we established the possibility of effective use of the AE method in chemical reactions of high-temperature oxidation using the example of combustion solid cellulose-containing materials [14,15].

The features of the combustion process of these materials, clearly marked on the amplitude-time characteristics (ATC) and frequency response function (FRF), allow the nature of the combustible material to be identified with sufficient accuracy. Therefore, in subsequent researches, the AE method was first applied to research the effect of physicochemical properties on the high-temperature oxidation (combustion) kinetics of certain liquid OM of various classes, which are most used in the operation of critical infrastructure facilities.

In this regard, the purpose of this work is to establish the features of the ignition of liquid OM of various classes based on the results of determining the formation features ATC of the AE process, as well as analysis of the FRF and assessment of the fractal dimension of the acoustic signal of the combustion process. The following tasks were formulated:

1. Determination of the characteristic maximum (peaks) FRF  $A_m(f)$  of the acoustic signal of an active high-temperature redox process from the number of carbon atoms  $n(C)$  in the carbon skeleton of the OM molecule and their  $M$  molar mass.

2. Determination of the amplitude dependence of the  $A_m(f)$  characteristic peaks FRF and the  $D_\tau$  fractal dimension of the received acoustic signal on

the dynamics of the decay of the OM combustion process in time depending on  $n(C)$ .

3. Estimation  $\tau_1$  of the initial and  $\tau_2$  final burning times of the primary cloud of OM vapors, as well as the duration of  $\Delta\tau=\tau_2-\tau_1$  their burning, depending on  $n(C)$ .

4. Establishment of the relationship between the thermodynamic and kinetic parameters of the process of high-temperature oxidation (combustion) of some OM, depending on  $n(C)$  and  $P$  partial vapor pressure. It must be based on the results of the analysis of the acoustic signal FRF.

#### **Research methodology**

The analysis of the acoustic signal of the process of high-temperature oxidation (combustion) of OM, both at the stage of primary ignition and during the combustion reaction, is implemented in the article by converting the  $A(t)$  signal into a  $X=X_1, X_2, \dots, X_N$  numerical series followed by the application of the R/S-analysis fractal method [16]. That method based on the use of in the analysis of observations of the dimensionless indicator in the form of the ratio of the range  $R=x_{\max}-x_{\min}$  of the accumulated deviation from the mean to the standard deviation  $S$ .

The use of R/S-analysis to assess the  $X$  numerical series of an  $A(t)$  acoustic signal is due to the presence of a signal-to-noise ratio less than one, which is not a condition for the functioning of a normally distributed system or close to it. In this article, the fractal structure of the  $X$  time series was assessed as a combination of a background signal and the desired acoustic signal. This signal was obtained in the course of high-temperature oxidation (combustion) of organic matter.

Calculations of the  $D_\tau$  fractal dimension were performed for the first time, taking into account the features of acoustic spectrum for liquid OM systems subjected to high-temperature oxidation. The fractal dimension reflects the degree of similarity of the ATC of the analyzed liquid OM, and characterizes the dynamics of combustion and decay processes (for specimens of constant volume) [17]. Fractal dimension  $D_\tau$  (as the degree of break of the series) was determined as  $D_\tau=2-H$ , where  $H$  is the Hurst exponent. The  $H$  indicator was determined from the  $R/S=(\alpha A)^H$  condition, where  $A$  is the number of observation periods, and  $\alpha$  is a given constant, a positive number equal to 0.5 for a relatively short-term time series of natural effect.

Some alcohols ( $C_1$ ,  $C_2$ ,  $C_3$ ,  $C_4$ ,  $C_5$  and  $C_8$ ), their isomers ( $C_3$ ,  $C_5$  and  $C_8$ ), as well as hydrocarbon liquid ( $C_8$ ,  $C_{12}$ , and  $C_{16}$ ) were taken for the research. Rigorously selected samples of OM ( $V=2$  ml) were transferred into a 48 mm metal bowl in diameter and 5 mm in height. The bowl was equipped with an

electric non-contact and silent ignitor. A schematic of the laboratory setup is shown in Fig. 1, where an acoustic signal analyzer with an interference microphone is positioned at a  $\approx 100$  mm distance from the edge of the metal bowl. The electrical ignition and the acoustic microphone amplifier were switched on simultaneously. This allows recording the spectrograms at the primary stage of combustion (ignition) of OM vapors, and the process of combustion of the OM mass.

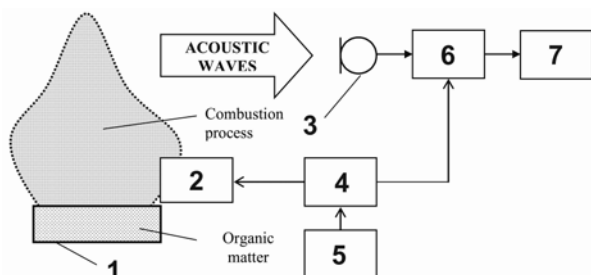


Fig. 1. Functional diagram of the installation for the research of acoustic waves of the combustion process of liquid OM: 1 – metal bowl with the analyzed OM; 2 – electrical ignitor; 3 – acoustic microphone; 4 – switch for synchronous activation of ignitor (2) and acoustic microphone (3); 5 – power supply; 6 – amplifier; and 7 – spectrum analyzer

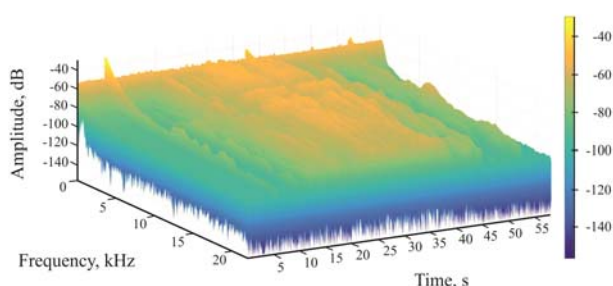


Fig. 2. Acoustic signal spectrogram of the high-temperature oxidation (combustion) of methanol

The results of laboratory researches are shown in Fig. 2. The graph of time variation spectrum of the received acoustic signal of the process high-temperature oxidation (combustion) of methanol was obtained in the course of the experiment.

Changes in the spectrum of the acoustic signal high-temperature oxidation (combustion) of OM from time were recorded until the complete cessation of combustion (no oscillatory of combustion) in the frequency range of 5–25000 Hz.

The results of processing the spectrograms of the acoustic signals of the high-temperature oxidation (combustion) process of various liquid organic matter types are shown in the graphs in the coordinates  $n(A_m(t))$  vs.  $n(C)$ ,  $n(A_m(f))$  vs.  $n(C)$ ,  $n(A_m(t))$  vs.  $M$

and  $n(A_m(f))$  vs.  $M$ . In addition, the results of acoustic signal fractal dimension calculations in coordinates  $D_\tau$  vs.  $n(C)$  were presented. Based on the results of determining (analysis of the FRF of the acoustic signal) of the  $\tau_1$  start and  $\tau_2$  end of the ignition the  $\tau_1$  vs.  $n(C)$ ,  $\tau_2$  vs.  $n(C)$  and  $\Delta\tau$  vs.  $n(C)$  dependences were made.

### Results and discussion

A working hypothesis for processing and analyzing the results of research the process of high-temperature oxidation (combustion) of some OM by the AE method is based on the assumption that the nature of the ATC and FRF depends from the physicochemical constants of the combustible substance ( $T_f$  is the flare temperature;  $T_{ign.}$  is the ignition temperature;  $T_{sp.ign.}$  is the auto-ignition temperature;  $\Delta T$  is the temperature flame propagation interval;  $P$  is the partial pressure of OM vapors over the solvent;  $\Delta\tau$  is the burning time of the primary cloud of OM vapors;  $\Delta H_0^\circ$  is the standard enthalpy of formation of a combustible substance; and  $\Delta H_\tau^\circ$  is the standard enthalpy of high-temperature oxidation of the combustible substance). To substantiate this hypothesis, it is necessary to establish the relationship between the physicochemical constants (the number of carbon atoms in a molecule, the effects of isomerism) and the molar mass of the investigated OM. For this, the equations of OM combustion reactions were drawn up and the values  $\Delta H_0^\circ$  and  $\Delta H_\tau^\circ$  were calculated (Table 1).

Analysis of the calculation results (Table 1) made it possible to establish an unambiguous dependence of the increase in the heat of formation of (n-) normal and (iso-) isomers ( $C_1$ – $C_8$ ) alcohols and “heavier” ( $C_8$ ,  $C_{12}$ ,  $C_{16}$ ) hydrocarbons from the number of carbon atoms in the skeletal framework.

Based on the presence of  $\Delta H_0^\circ$  and  $\Delta H_\tau^\circ$  dependences indexes of the OM combustion processes samples of constant volume on  $n(C)$  and  $M$  indexes, it was suggested that there are similar dependences of the FRF of the acoustic signal during the combustion of OM samples on the  $n(C)$  and  $M$  indexes of these substances. According to Table 1, the  $\Delta H_\tau^\circ$  values for alcohol isomers are greater than for aliphatic n-alcohols. Respectively, the values for alcohol isomers are lower, although insignificantly. The established facts for the considered regularities unambiguously indicate the complexity of the high-temperature oxidation process of the alcohol isomers under research.

One of the identifying factors of the nature of OM during their high-temperature oxidation is that for alcohol isomers the period repetition maximum  $A$  of the acoustic signal should be shorter than for n-alcohols.

Table 1

The value of the energies of ( $\Delta H_0^\circ$ ) formation and ( $\Delta H_\tau^\circ$ ) standard heat effects of the high-temperature oxidation (combustion) reactions of ( $C_1$ – $C_8$ ) aliphatic alcohols and ( $C_{12}$ – $C_{16}$ ) heavy liquid hydrocarbon

No.	Reaction equations for high-temperature oxidation (combustion) of various OM	$\Delta H_0^\circ$ , $\frac{\text{kJ}}{\text{mol}}$	$\Delta H_\tau^\circ$ , $\frac{\text{kJ}}{\text{mol}}$
1	$\text{CH}_3\text{OH} + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}$	-201.3	-763.8
2	$\text{C}_2\text{H}_5\text{OH} + 3\text{O}_2 = 2\text{CO}_2 + 3\text{H}_2\text{O}$	-234.9	-1408.0
3	$n\text{-C}_3\text{H}_7\text{OH} + 4.5\text{O}_2 = 3\text{CO}_2 + 4\text{H}_2\text{O}$	-257.7	-2067.4
4	$\text{iso-C}_3\text{H}_7\text{OH} + 4.5\text{O}_2 = 3\text{CO}_2 + 4\text{H}_2\text{O}$	-272.4	-2051.4
5	$n\text{-C}_4\text{H}_9\text{OH} + 6\text{O}_2 = 4\text{CO}_2 + 5\text{H}_2\text{O}$	-274.6	-2728.0
6	$\text{iso-C}_4\text{H}_9\text{OH} + 6\text{O}_2 = 4\text{CO}_2 + 5\text{H}_2\text{O}$ (secondary)	-292.6	-2713.0
7	$n\text{-C}_5\text{H}_{11}\text{OH} + 7.5\text{O}_2 = 5\text{CO}_2 + 6\text{H}_2\text{O}$	-302.5	-3383.6
8	$\text{iso-C}_5\text{H}_{11}\text{OH} + 7.5\text{O}_2 = 5\text{CO}_2 + 6\text{H}_2\text{O}$ (tertiary)	-330.0	-3353.0
9	$n\text{-C}_8\text{H}_{17}\text{OH} + 12\text{O}_2 = 8\text{CO}_2 + 9\text{H}_2\text{O}$	-357.0	-5360.0
10	$\text{iso-C}_8\text{H}_{17}\text{OH} + 12\text{O}_2 = 8\text{CO}_2 + 9\text{H}_2\text{O}$	-367.6	-5352.3
11	$\text{C}_8\text{H}_{18}(\text{g.,liq.}) + 12.5\text{O}_2 = 8\text{CO}_2 + 9\text{H}_2\text{O}$	-215.5 (g.) -259.3 (liq.)	-5505.1 (g.) -5496.5 (liq.)
12	$\text{C}_{12}\text{H}_{26}(\text{g.}) + 18.5\text{O}_2 = 12\text{CO}_2 + 13\text{H}_2\text{O}$ ( $M=172.3 \div 204.0$ )	-290.9	-8147.2
13	$\text{C}_{16}\text{H}_{34}(\text{g.}) + 24.5\text{O}_2 = 16\text{CO}_2 + 17\text{H}_2\text{O}$ ( $C_{13}$ – $C_{15}$ ; $C_{12}$ – $C_{16}$ ; $M=198 \div 199$ )	-373.3	-10782.2
14	$\text{C}_3\text{H}_6\text{O} + 4\text{O}_2 = 3\text{CO}_2 + 3\text{H}_2\text{O}$ (acetone)	-217.6	-1821.4

Since the beginning of the high-temperature oxidation liquid and solid OM process occurs through the primary stage (the ignition of a gaseous cloud (vapors) above the solvent) the ignition (flash) time is determined by the P vapor pressure of hydrocarbons at standard temperatures (Fig. 3) and  $\Delta T$  values (Table 2).

According to Table 2, an increase in  $n(C)$  or  $M$  of ( $n$ - and  $\text{iso}$ -) alcohols an increase in  $T_f$  and  $T_{\text{ign}}$  is observed. In this case, these values for  $\text{iso}$ -alcohols are somewhat lower than for  $n$ -alcohols and the  $\Delta T$  values in the series of alcohols under research practically change little, but there is a shift in the value of the  $\Delta T$  interval with increasing  $n(C)$  or  $M$  towards high temperatures at  $n(C) > 10$ .

Those are “heavier” ( $C_8$ ,  $C_{12}$ ,  $C_{16}$ ) hydrocarbons, than alcohols. It is natural to assert that the higher the vapor pressure, the faster the primary ignition (flash) occurs when the  $T_{\text{ign}}$  temperature of the ignition level is reached and the faster the primary gaseous mass of the OM vapors should burn. However, at a lower  $P$ , the higher is the flashes point of the OM vapors and the longer is the time interval of the stage primary ignition of the OM.

Figure 4 shows the  $\tau_1$  and  $\Delta\tau$  values calculated by ATC for alcohols, ketone and hydrocarbon (all substances being in the liquid phase). Here, the practically insignificant effect of alcohol isomerism on  $\tau_1$ ,  $\tau_2$  and  $\Delta\tau$  values depending on the number of C (atoms in the framework of  $\text{iso}$ -alcohol molecules) is clearly observed.

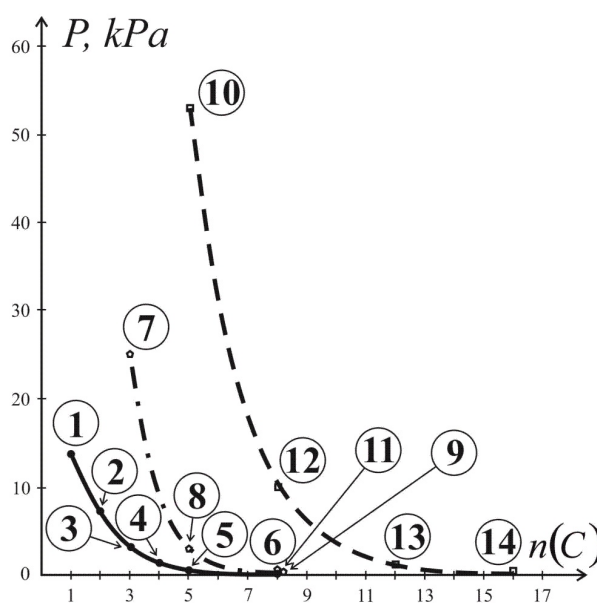


Fig. 3. Partial vapor pressure of liquid OM (at 20°C) as a function of  $n(C)$  in the carbon skeleton molecules. Legend: alcohols (·): 1 –  $\text{CH}_3\text{OH}$ ; 2 –  $\text{C}_2\text{H}_5\text{OH}$ ; 3 –  $\text{iso-C}_3\text{H}_7\text{OH}$ ; 4 –  $n\text{-C}_4\text{H}_9\text{OH}$ ; 5 –  $\text{iso-C}_5\text{H}_{11}\text{OH}$ ; 6 –  $\text{iso-C}_8\text{H}_{17}\text{OH}$ ; ketones (Ж%): 7 – propanone ( $\text{C}_3\text{H}_6\text{O}$ ); 8 – pentanone ( $\text{C}_5\text{H}_{10}\text{O}$ ); 9 – octanone ( $\text{C}_8\text{H}_{16}\text{O}$ ); hydrocarbon (У%): 10 – pentane ( $\text{C}_5\text{H}_{12}$ ); 11 – octane ( $\text{C}_8\text{H}_{18}$ ); 12 – gasoline ( $\text{C}_8\text{H}_{18}$ ); 13 – diesel fuel ( $\text{C}_{12}\text{H}_{28}$ ); and 14 – paraffin ( $\text{C}_{16}\text{H}_{34}$ )



Table 2

**Values of  $T_f$ ,  $T_{ign.}$ ,  $T_{sp.ign.}$  and temperature limits of flame spread temperature limits of organic matters for the high-temperature oxidation (combustion) reaction**

No.	OM formula	$T_f$ , °C		$T_{ign.}$ , °C	$T_{sp.ign.}$ , °C	Flame spread. Temperature limits, °C		
						lower	upper	$\Delta T$
1	CH <sub>3</sub> OH	6.0	–	13.0	440	5	39	34
2	C <sub>2</sub> H <sub>5</sub> OH	13.0 (c.p.)*	16.0 (o.p.)	18.0	400	11	41	30
3	n-C <sub>3</sub> H <sub>7</sub> OH	23.0 (c.p.)	29.0 (o.p.)	30.0	371	21	55	34
4	iso-C <sub>3</sub> H <sub>7</sub> OH (2-propanol)	14.0 (c.p.)	18.0 (o.p.)	21.0	430	11	42	31
5	n-C <sub>4</sub> H <sub>9</sub> OH	35.0 (c.p.)	41.0 (o.p.)	43.0	340	34	67	33
6	iso-C <sub>4</sub> H <sub>9</sub> OH (secondary)	24.0	–	32.0	395	20	55	35
7	n-C <sub>5</sub> H <sub>11</sub> OH	48.0	–	57.0	300	45	79	34
8	iso-C <sub>5</sub> H <sub>11</sub> OH (tertiary)	24.0	–	34.0	410	23	55	32
9	n-C <sub>8</sub> H <sub>17</sub> OH	86.0	–	92.0	260	80	116	36
10	iso-C <sub>8</sub> H <sub>17</sub> OH (iso-octanol)	77.0 (c.p.)	82.0 (o.p.)	86.0	266	70	108	38
11	C <sub>8</sub> H <sub>18</sub> (liq.)	14.0	–	19.0	215	13	49	36
12	C <sub>12</sub> H <sub>26</sub> (liq.) (M=172÷20)	37.0 65.0–110.0	59.0	112.0	210–370	35 99	92 155	57 56
13	C <sub>16</sub> H <sub>34</sub> (liq.) C <sub>13</sub> –C <sub>15</sub> ; (M=181÷212)	–	95.0 (o.p.)	116	190	83	146	63
	C <sub>12</sub> –C <sub>16</sub> ; (M=172÷226)	98.0 (c.p.)	107.0 (o.p.)	112	200	95	145	50
14	C <sub>3</sub> H <sub>6</sub> O acetone (ketone)	–18.0 (c.p.)	–9.0 (o.p.)	–5	535 (in air) 485 (in atm. O <sub>2</sub> )	–20	6	26

Note: \* – c.p. – closed pot; o.p. – open pot.

The observed phenomena can be explained by the level of discrepancy between  $T_f$  and  $T_{ign.}$  temperatures n- and iso-alcohols (Table 2). In the case of hydrocarbon with a C high content at ordinary temperatures, their P values are approximately equal to zero, Therefore, heating is preliminary required (for paraffin, preheating and transition to the liquid phase) until a minimum volume of the gas phase of hydrocarbon is formed sufficient for ignition (flash) and subsequent combustion. Due to this, the results of calculating  $\tau_1$ ,  $\tau_2$  and  $\Delta\tau$  for (C<sub>12</sub>H<sub>36</sub>–C<sub>14</sub>H<sub>30</sub>) diesel fuel and (C<sub>16</sub>H<sub>34</sub>–C<sub>18</sub>H<sub>38</sub>) paraffin are destructive in the case of analysis  $\tau_1$  vs. n(C),  $\tau_2$  vs. n(C) and  $\Delta\tau$  vs. n(C) general dependences, but in the context of analysis of  $n(A_m(t))$  vs. n(C),  $n(A_m(t))$  vs. M,  $n(A_m(f))$  vs. n(C) and  $n(A_m(f))$  vs. M dependences for series alcohols and hydrocarbons can be considered.

Based on the dependences of the number of  $n(A_m(t))$  amplitude maximum and  $n(A_m(f))$  on n(C),

calculated from ATC and FRF of the acoustic signal, we established the difference in the  $n(A_m(t))$  and  $n(A_m(f))$  values of aliphatic and isomeric structures of alcohols, as well as «heavier» hydrocarbons depending on n(C) and M.

Taking into account that the amplitude of the spectrum characterizes the power of acoustic radiation is determined by the amount of oxidized fuel per unit of time, that it can be assumed that the power of the emission process decreases with an increase in n(C) or M (Figs. 5 and 6).

It follows from the presented analysis of the experimental result that the parameters of the acoustic signal amplitude modulation and its amplitude-frequency depend on the number of carbon atoms (n(C)) in the carbon skeleton of molecules (Fig. 5) and the M value molar mass (Fig. 6). In this work, the dependences  $n(A_m(t))$  and  $n(A_m(f))$  on M were approximated by a linear function, which does not

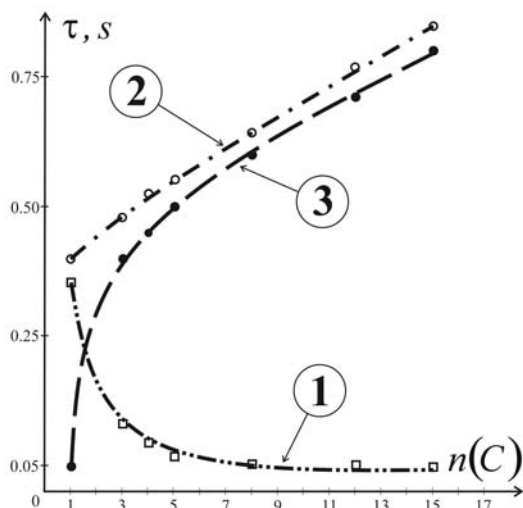


Fig. 4. Time values: flash beginning ( $\tau_1$ ), flash ending ( $\tau_2$ ) and the duration of the flash (combustion of the primary layer of OM vapors) ( $\Delta\tau$ ) for the investigated alcohols, ketones and hydrocarbon: 1 –  $\tau_1$ ; 2 –  $\tau_2$ ; and 3 –  $\Delta\tau$

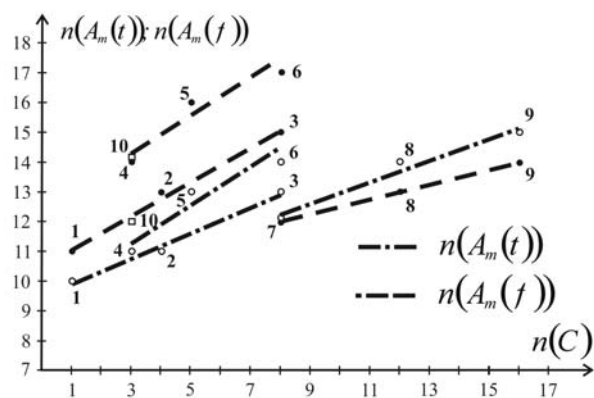


Fig. 5. The change in the number of  $n(A_m(t))$  amplitude maximum (in the time interval from ignition to complete combustion termination) and  $n(A_m(f))$  (in the 5–25000 Hz frequency range) in the acoustic signal during the course of the high-temperature oxidation (combustion) reaction of alcohols, ketone and hydrocarbon as a function of  $n(C)$  in hydrocarbon skeleton of liquid OM. OM designations: 1 –  $\text{CH}_3\text{OH}$ ; 2 –  $n\text{-C}_4\text{H}_9\text{OH}$ ; 3 –  $n\text{-C}_8\text{H}_{17}\text{OH}$ ; 4 –  $\text{iso-C}_3\text{H}_7\text{OH}$ ; 5 –  $\text{iso-C}_5\text{H}_{11}\text{OH}$ ; 6 –  $\text{iso-C}_8\text{H}_{17}\text{OH}$ ; 7 –  $\text{C}_8\text{H}_{18}$ ; 8 –  $\text{C}_{12}\text{H}_{26}$ ; 9 –  $\text{C}_{16}\text{H}_{34}$ ; and 10 –  $\text{C}_3\text{H}_6\text{O}$  (acetone)

contradict the law of effective masses for chemical reactions (for the high-temperature oxidation (combustion) reaction of OM).

Meanwhile, there are significant quantitative differences in the nature of  $n(A_m(t))$  and  $n(A_m(f))$  on  $n(C)$  and  $M$  dependences:  $n(A_m(t))$  and  $n(A_m(f))$  values for alcohol isomers turn out to be larger than those for  $n$ -alcohols. When passing from alcohols to «heavier» hydrocarbon (at  $n(C) \geq 8$  or  $M \geq 120$ –

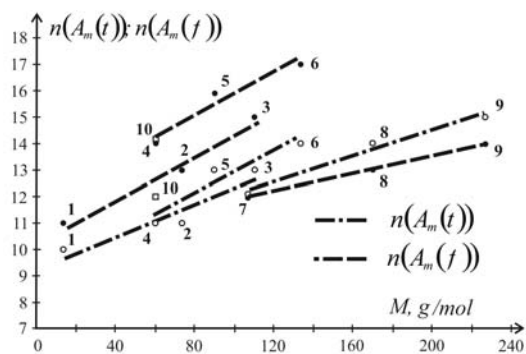


Fig. 6. The change in the number of  $n(A_m(t))$  amplitude maximum (in the time interval from ignition to complete combustion termination) and  $n(A_m(f))$  (in the 5–25000 Hz frequency range) in the acoustic signal during the course of the high-temperature oxidation (combustion) reaction of alcohols, ketone and hydrocarbon as a function of  $M$  (molar mass of the OM). OM designations: 1 –  $\text{CH}_3\text{OH}$ ; 2 –  $n\text{-C}_4\text{H}_9\text{OH}$ ; 3 –  $n\text{-C}_8\text{H}_{17}\text{OH}$ ; 4 –  $\text{iso-C}_3\text{H}_7\text{OH}$ ; 5 –  $\text{iso-C}_5\text{H}_{11}\text{OH}$ ; 6 –  $\text{iso-C}_8\text{H}_{17}\text{OH}$ ; 7 –  $\text{C}_8\text{H}_{18}$ ; 8 –  $\text{C}_{12}\text{H}_{26}$ ; 9 –  $\text{C}_{16}\text{H}_{34}$ ; and 10 –  $\text{C}_3\text{H}_6\text{O}$  (acetone)

130 g/mol), a peculiar reversibility of the location dependences is observed:  $n(A_m(f))$  vs.  $n(C)$  passes below of  $n(A_m(t))$  vs.  $n(C)$  (Fig. 5). A similar arrangement of these indicators is observed in the case of considering them depending on the  $M$  (Fig. 6).

The observed dependences in the mutual arrangement of the amplitude maximum for alcohols ( $n$ - and  $\text{iso}$ -) and «heavier» hydrocarbon can be explained by a change in the structure of alcohols and the absence of ( $\text{C}_8$ ,  $\text{C}_{12}$ ,  $\text{C}_{16}$ ) functional groups of hydrocarbon. It is possible to change the dynamics of combustion hydrocarbons, and accordingly, the type of amplitude modulation and spectral harmonics of the acoustic signal under the effect of the high-temperature oxidation process liquid OM. The reversibility of the mutual arrangement of  $n(A_m(t))$  and  $n(A_m(f))$  on  $n(C)$  and  $M$  dependences is observed (Figs. 5 and 6) due to the possible appearance of the listed factors.

The stated results of experimental researches allow creating a data bank of AEM–fire hazardous condition systems of critical infrastructure objects with flammable various nature liquids. In the case of a fire at a critical infrastructure facility, the AEM-system will allow real-time identification (by the presence of information on the FRF of OM combustion in the database) the nature and coordinates of the fire source. This information will be to support the adoption of anti-crisis decisions.

In order to increase the reliability and validity of the determining nature OM results (during high-temperature oxidation (combustion)), it is necessary

to obtain the results of testing the repeatability nature in time ( $t$ ) of the amplitude modulation maximum of the acoustic signal during the combustion specimens of various nature OM. To this end, the results of calculating the Hurst exponents ( $H$ ) and  $D_\tau$  fractal dimension were presented in Fig. 7.

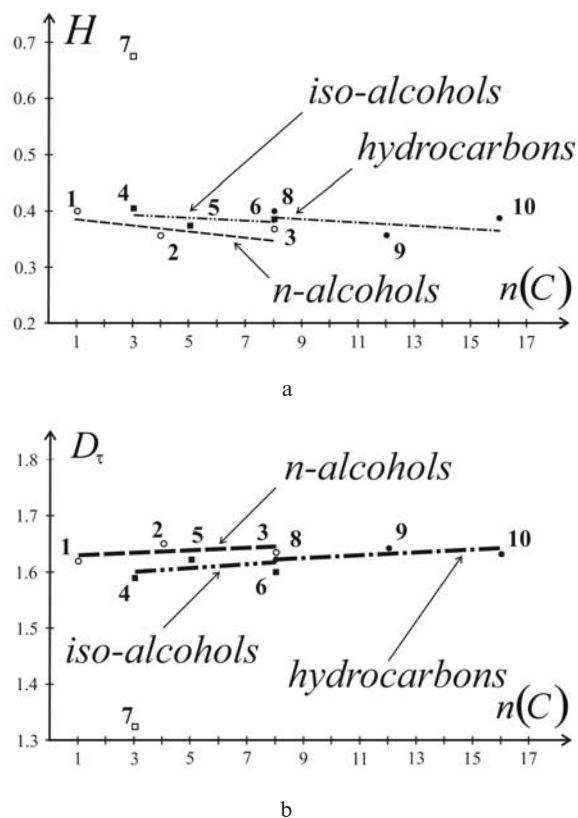


Fig. 7. Dependences of the change in the Hurst exponent ( $H$ ) – (a) and fractal dimension ( $D_\tau$ ) – (b) amplitude acoustic signal modulation of the high-temperature oxidation (combustion) reaction of some liquid OM on  $n(C)$ .

OM designations: 1 –  $\text{CH}_3\text{OH}$ ; 2 –  $n\text{-C}_4\text{H}_9\text{OH}$ ; 3 –  $n\text{-C}_8\text{H}_{17}\text{OH}$ ; 4 –  $\text{iso-C}_3\text{H}_7\text{OH}$ ; 5 –  $\text{iso-C}_5\text{H}_{11}\text{OH}$ ; 6 –  $\text{iso-C}_8\text{H}_{17}\text{OH}$ ; 7 –  $\text{C}_3\text{H}_6\text{O}$  (acetone); 8 –  $\text{C}_8\text{H}_{18}$ ; 9 –  $\text{C}_{12}\text{H}_{26}$  and 10 –  $\text{C}_{16}\text{H}_{34}$

It was found that, regardless of the nature ( $n(C)$ ) of the OM, the values of the  $H$  and  $D_\tau$  indexes for the investigated series of flammable liquids are in the following ranges:  $H=0.3\div 0.4$  and  $D_\tau=1.55\div 1.65$ . In addition, a tendency for the  $H$  and values to increase, respectively, was observed with a decrease in the  $D_\tau$  value for alcohol isomers (by about 0.05 units). According to the absolute  $H$  index value, the combustion process of the researched OM is antipersistent (temporary). The reaction of high-temperature oxidation of acetone ( $\text{C}_3\text{H}_6\text{O}$ ) is persistent (long-term), but not dynamic. Only when  $1 < H < 2$ ,

the combustion process acquires a dynamic character, however, it can be realized only if the OM mass is constant during the combustion time.

The practical constancy of values of the indicators  $H$  and  $D_\tau$  (Fig. 7) for the researched range OM indicates a sufficient degree of reliability and validity of the obtained dependence results of the high-temperature oxidation (combustion) process FRF and ATC liquid OM on physicochemical constants of combustible substance (Figs. 5 and 6). Therefore, the results of these graphical constructions can be recommended as information material for the reference data bank of the AEM–system of the fire hazardous state of critical infrastructure objects with flammable various nature liquids.

The complex representation proposed in Figs. 5–7 will increase the degree of early fire detection and reduce the likelihood of false device alarms for detecting the fire hazardous situation. This was based on the implementation of the acoustic emission effect.

### Conclusions

1. The method was proposed for diagnostics of the high-temperature oxidation (combustion) process organic ( $n(C)=1\div 8$ ) liquid alcohols and hydrocarbon ( $n(C)=8, 12$ , and 16). It is based on the research of dynamic parameters (type of amplitude modulation of the acoustic signal, amplitude-frequency characteristic, rigidly defined features of the structure of normal alcohols and their isomers and normal hydrocarbon  $n(C)$  the number of hydrocarbon atoms in the skeleton of the researched organic substances molecules or the molar mass ( $M$ ) value substances).

2. It was found that the dynamics of the high-temperature oxidation (combustion) process is associated with the  $n(A_m(t))$  maximum number and  $n(A_m(f))$  the amplitude-time and response-frequency functions of the acoustic signal and is determined by the physical ( $T_f$ ,  $T_{\text{ign}}$ ,  $T_{\text{sp ign}}$ ,  $\Delta T$ ,  $P$ ), physicochemical thermodynamic parameters ( $\Delta H_0^\circ$ ,  $\Delta H_\tau^\circ$ ) of the process is described by linear dependences on  $n(C)$  and  $M$  organic substances.

3. Using the method of acoustic emission, the «flash» effect (the time of the primary combustion process of vapors liquid organic substances) was first researched. An unambiguous dependence of the duration of this process ( $\Delta\tau$ ) on the partial vapor pressure over the pure solvent and the flash point ( $T_f$ ) or ignition ( $T_{\text{ign}}$ ) was established. It was found that the larger  $P$  and the smaller  $T_f$  ( $T_{\text{ign}}$ ), the shorter  $\Delta\tau$  «flash» time is.

4. With the help of the developed algorithm and software for processing the parameters of the acoustic signal by (Hurst exponent) and  $D_\tau$  fractal

dimension, it was found that regardless of the nature of the investigated organic substances ( $n(C)=1\div 16$ ), the  $H$  and  $D_r$  values of the indexes remain constant for the investigated series of flammable liquids ( $H=0.3\div 0.4$ ;  $D_r=1.55\div 1.65$ ). At the same time, the tendency of an increase in  $H$  and  $D_r$  indexes, accordingly, a decrease in  $D_r$  index for alcohol isomers was established (by approximately 0.05 units). The practical constancy of the  $H$  and  $D_r$  parameters for organic substances with a linear and isomeric structure indicates the corresponding degree of reliability and validity of the obtained results processing acoustic signals under the effect of high-temperature oxidation (combustion) reaction of some organic substances, which makes it possible to reduce the rate of false alarms of the acoustic device detecting fires at critical infrastructure facilities and establishing the nature of combustible material in the fire seat.

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**ВИЯВЛЕННЯ ПРИРОДИ ЕФЕКТІВ АКУСТИЧНОЇ ЕМІСІЇ ПРОЦЕСУ ВИСОКОТЕМПЕРАТУРНОГО ОКИСЛЕННЯ (ГОРІННЯ) ДЕЯКИХ РІДКИХ ОРГАНІЧНИХ РЕЧОВИН**

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У роботі вперше наведені результати дослідження впливу фізико-хімічних характеристик деяких органічних речовин на кінетику їх високотемпературного окислення (горіння), які отримані методом реєстрації спектрів акустичної емісії від осередку спалаху. Результати дослідження амплітудно-часових характеристик (до повного затухання горіння) та амплітудно-частотні характеристики (у заданому діапазоні частот) процесу горіння рідких органічних речовин показали однозначну залежність: 1) кількості у заданому діапазоні частот амплітудних максимумів частотного спектра прийнятого акустичного сигналу, а також фрактальної розмірності прийнятого акустичного сигналу, від кількості атомів вуглецю в вуглецевому каркасі органічних речовин та їх молярної маси; 2) часу початку горіння (спалаху) первинної хмари пари органічних речовин і кінцевого часу горіння первинної хмари парів органічних речовин від кількості атомів вуглецю в вуглецевому каркасі органічних речовин і парціального тиску пари органічних речовин. Практичний аспект використання отриманих результатів продиктований необхідністю напрацювання стандартних зразків амплітудно-часових та амплітудно-частотних характеристик в залежності від фізико-хімічних і горючих властивостей органічних речовин, які необхідні для банку даних системи акустико-емісійного моніторингу надзвичайних ситуацій і прийняття антикризових управлінських рішень на об'єктах критичної інфраструктури.

**Ключові слова:** високотемпературне окислення, горіння, акустично-емісійний аналіз, фізико-хімічні характеристики, амплітудно-частотні характеристики, надійність, спектрограма, акустико-емісійний моніторинг.

**ESTABLISHING THE NATURE OF KINETIC EFFECTS OF THE HIGH-TEMPERATURE OXIDATION (COMBUSTION) PROCESS OF SOME LIQUID ORGANIC MATTERS BY ACOUSTIC RADIATION**

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In this article, the results of the study on the physicochemical characteristics of some liquid organic matters on the kinetics of their high-temperature oxidation (combustion) were presented for the first time. These results were obtained by the method of acoustic emission spectrum from heat source. The research results of the amplitude-time characteristics (until cessation of combustion completely) and the frequency response functions (in a given frequency range) of oxidation (combustion) process of liquid organic matters showed that there are following unambiguous dependences: 1) the dependences of the number of the amplitude maximum of the frequency and time spectrum in a given frequency range, as well as of the fractal dimension of the received acoustic signal on the number of carbon atoms in the carbon frame of organic matters and their molar mass; and 2) the dependences of the time of beginning of the combustion (ignition) of primary cloud of organic matters vapors and the final combustion time of the primary cloud of organic matters vapors on the number of carbon atoms in the carbon frame of the organic matters and their partial vapor pressures. The practical aspect of using the results obtained is dictated by the need to develop standard samples of amplitude-time and amplitude-frequency characteristics, depending on the physicochemical and combustible properties of the organic matters. This is necessary for the data bank of the acoustic emission monitoring system to establish a fire hazardous state and make anti-crisis decisions at critical infrastructure facilities.

**Keywords:** high-temperature oxidation; combustion; acoustic emission analysis; physicochemical characteristics; frequency response functions; reliability; spectrogram; acoustic emission monitoring.

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